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METHOD FOR PRODUCING ACETOL

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The invention concerns a method for producing acetol by dehydration of glycerol at elevated temperatures. It is proposed, as an industrially usable method with high yields and conversions, that glycerol be converted to acetol and water with a heterogeneous hydrogenation/dehydrogenation catalyst that contains an element of the first and/or eighth side group, at temperatures between 180 and 400°C.

The invention concerns a method for producing acetol by dehydration of glycerol at elevated temperatures.

Acetol or hydroxyacetone is used, among other places, as a reducing agent in dying with vat dyes (the newspaper *Textil Praxis International*, 1989, p. 737). It is also a starting material

for synthesis of heterocycles and can be used, for example, for enzymic production of R-(-)-1,2-propanediol (DE 38 30 253 A1).

On an industrial scale, acetol is mainly obtained by catalytic oxidation, starting from 1,2-propanediol (Chem. Eng. News 43 (1965)) or by dehydrogenation of 1,2-propanediol (DE 23 13 957 B).

However, a method that starts from glycerol as the starting material would also be of economic interest. The dehydration of glycerol at temperatures between 430 and 450°C is known ("Liebigs Annalen der Chemie," 1904, Vol. 335, pp. 209-223). Here glycerol is slowly passed through a heated pumice-packed tube. The experiment takes roughly 16 h if 250 g glycerol is used. One obtains a great deal of graphite and a brownish distillate, which contains acetol, water, formaldehyde, acetaldehyde, acrolein, unreacted glycerol and other substances. Fractional distillation is necessary to recover aqueous acetol or nearly water-free acetol from the reaction mixture. Such a method is not suitable for large scale use. Only 73% of the input glycerol is converted and only 7.5% acetol appears in the end in the reaction mixture, as can be learned from the figures in said article. Moreover, the reaction progresses very slowly.

For this reason, the invention is based on the task of improving the method mentioned above so that it is industrially usable and allows considerably higher yields and conversions. The reaction mixture should contain mainly acetol and water and have only negligible quantities of by-products.

This task is solved in accordance with the invention by converting glycerol to acetol and water with a heterogeneous hydrogenation/dehydrogenation catalyst that contains an element of the first and/or eighth side group, at temperatures between 180 and 400°C.

The conversion of glycerol is between 85 and 99.8% and the selectivity for acetol is surprisingly high, between 60 and 85%. Relatively high space-time yields are achieved. Propanediol is also formed in smaller quantities as an intermediate product. Glycerol oligomers are not detectable. Also, the disadvantages of the known method that are mentioned above no longer arise in accordance with the invention.

Conversions and selectivity are especially high if water-free glycerol is used. Still better results are obtained if the glycerol is diluted with a short-chain secondary alcohol, in particular isopropanol. The isopropanol can easily be separated from the reaction mixture.

In particular, it is proposed that the reaction be carried out at temperatures between 240 and 300°C, especially at about 280°C.

Preferably, the catalyst contains copper, in particular, finely divided copper or copper oxide on a support. The use of copper chromite, copper-zinc oxide, copper silicate, copper-aluminum oxide or combinations thereof, possibly with promoters, is also advantageous.

It is of interest from the economic standpoint that the method is carried out at pressures under 20 bar.

In particular, for industrial use it is advantageous if the catalyst is in the form of a fixed bed. The liquid throughput per hour and per catalyst volume in this case is between 0.1 and 10 h^{-1}. The reaction temperature can be controlled and adjusted particularly readily if the process is carried out in a tubular reactor. However, the use of other types of reactors is also possible.

In another advantageous embodiment, unreacted glycerol and possibly the added short-chain secondary alcohol are recycled back to the input product.

In the following examples of the invention are described in more detail. The invention is, however, not limited to these examples.

Example 1

1 L of catalyst (Cu chromite type, 0203T, tablets 4 mm in diameter and thickness, product of the Engelhard Co.) was put into a thermal oil-heated reaction tube, dried, and reduced with 1% hydrogen in nitrogen at a temperature between 150°C and 200°C. Then the catalyst was heated to 260°C under a stream of nitrogen at 0.5 Nm^3/h. 310 mL aqueous glycerol containing 80 wt% glycerol was fed at LHSV 0.25 h^{-1} by means of a pump via a preheater. The experiment was carried out without pressure, i.e., at atmospheric pressure. The resulting reaction mixture was cooled. The condensed components were collected in a separator.

The reaction mixture contained, wt%: 13.5% unreacted glycerol, 30.1% acetol, 4.0% propanediol, 12.7% unidentified water-soluble components, and 34% water.

Example 2

The experiment was repeated as in Example 1. However, the reactor was heated to 280°C. The reaction mixture contained, wt%: 7.2% unreacted glycerol, 36.4% acetol, 3.6% propanediol, 11.5% unidentified water-soluble components, and 35% water.

Example 3

The experiment was carried out as in Example 1. However, 1000 mL/h 80% aqueous glycerol was supplied. The analysis gave, wt%: 9.9% unreacted glycerol, 24.8% acetol, 7.4% propanediol, 6.6% unidentified water-soluble components, and 38% water.

Example 4

Under otherwise similar conditions to Example 1, the reactor was heated to 280°C and 1000 mL 80% aqueous glycerol was used. The analysis showed 9.0% glycerol, 30.7% acetol, 4.8% propanediol, 8.7% unidentified components, and 38% water.

Example 5

Under otherwise similar conditions to Example 1, the reactor was heated to 300°C and 310 mL 80% aqueous glycerol was used. The analysis gave, wt%: 0.3% glycerol, 18.5% acetol, 1.3% propanediol, 9.3% unidentified water-soluble components, and 41.3% water.

Examples 6-11

Under otherwise similar conditions to Example 1, 99.5 wt% glycerol was used and the reaction was carried out at various temperatures and throughputs. Analysis results are summarized in Table 1.

Examples 12-14

Under otherwise similar conditions to Example 1, 99.5 wt% glycerol was diluted with isopropanol in an 80:20 ratio by weight, and the reaction was carried out at various temperatures and throughputs. Analysis results are summarized in Table 2.

Table 1

Input: Glycerol (99.5 wt%)

	Example					
	6	7	8	9	10	11
Throughputs (mL/h)						
Glycerol	250	800	800	250	250	800
LHSV (1/h)	0.25	0.8	0.8	0.25	0.25	0.8
Reaction temperature (°C)	300	300	280	280	260	260
Composition of reaction mixture (wt%)						
Glycerol	<0.2	0.6	1.0	0.5	1.7	3.1
Acetol	29.6	38.0	42.8	46.0	47.6	43.6
1,2-Propanediol	1.4	2.5	3.2	2.2	3.6	6.3
Water	26.1	25.1	25.4	23.3	23.0	24.4
Unidentified water-soluble components	12.0	8.5	3.9	5.5	5.4	4.4
Remainder	30.7	25.6	23.7	23.5	18.7	18.3

Table 2

Input: Glycerol (80 wt%)/Isopropanol (20 wt%)

	Example 12	13	14
Throughputs (mL/h)			
Glycerol	250	250	320
Isopropanol	60	60	80
LHSV (1/h)	0.25	0.25	0.25
Reaction temperature (°C)	280	300	300
Composition of reaction mixture (wt%)			
Glycerol	<0.2	<0.2	<0.2
Acetol	53.6	51.1	52.2
1,2-Propanediol	1.8	1.5	1.4
Isopropanol	8.1	8.2	9.6
Water	18.4	19.4	19.6
Unidentified water-soluble components	7.4	8.8	6.4
Remainder	10.8	10.8	10.6

Claims

1. A method for producing acetol by dehydration of glycerol at elevated temperatures, characterized by the fact that glycerol is converted to acetol and water with a heterogeneous hydrogenation/dehydrogenation catalyst containing an element of the first and/or eighth side group, at temperatures between 180 and 400°C.

2. A method as in Claim 1, characterized by the fact that water-free glycerol is used.

3. A method as in Claim 1 or 2, characterized by the fact that the glycerol that is used is diluted with a short-chain secondary alcohol, in particular isopropanol.

4. A method as in one of Claims 1-3, characterized by the fact that the reaction is carried out at temperatures between 240 and 300°C, in particular at about 280°C.

5. A method as in one of Claims 1-4, characterized by the fact that the catalyst contains copper, in particular, finely divided copper or copper oxide on a support.

6. A method as in one of Claims 1-5, characterized by the fact that the reaction is carried out at pressures under 20 bar.

7. A method as in one of Claims 1-6, characterized by the fact that the catalyst is in the form of a fixed bed and the liquid throughput per hour catalyst volume is between 0.1 and 10 h^{-1}.

8. A method as in one of Claims 1-7, characterized by the fact that unreacted glycerol and, optionally, the added short-chain secondary alcohol are recycled back to the input product.